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(54) HYDROGENATING CATALYST FOR HEAVY OIL AND HYDROGENATING METHOD OF HEAVY OIL USING THE SAME

(57)Abstract:

PURPOSE: To impart enough hydrogenation activity to a catalyst for hydrogenating of heavy oil and to enable use of recovered oil which is not decomposed as a fuel by depositing a compd. of group VIA metal or VIII iron group metal in the Periodical Table on a specified coal or cellulose base org. material.

CONSTITUTION: A compd. of group VIA metal or VIII iron group metal in the Periodical Table is deposited on a coal containing <65wt.% carbon in terms of an anhydrous ash-free base body or on a cellulose-base org. material. As for the coal, peat and grass peat (such as peat moss) are especially preferable. As for the cellulose-base org. material, wood, paper, pulp, chip, woody fiber or plant fiber are used, and especially pulp, chip, and paper are preferable. Thereby, enough activity and performance are obtd. for hydrogenation of various kinds of heavy oils. Moreover, without decomposing and removing the catalyst, the recovered oil not decomposed yet can be preferably used as a fuel fr the boiler.

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* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The catalyst for hydrogen treatings of the heavy oil to which the rate of the carbon in a dry ash free basis supports the compound of a periodic-table VIA group metal, and/or the compound of a periodic-table VIII group's iron-group metal at least to the coal or the cellulose system organic substance which is 65 or less % of the weight, and is characterized by the bird clapper.
[Claim 2] The catalyst for hydrogen treatings according to claim 1 whose aforementioned coal is peat or grass peat.
[Claim 3] The catalyst for hydrogen treatings according to claim 1 whose aforementioned cellulose system organic substance is wood, pulp, a chip, paper, woody fiber, or a vegetable fiber.
[Claim 4] The catalyst for hydrogen treatings according to claim 1 or 3 whose aforementioned cellulose system organic substance is pulp, a chip, or paper.
[Claim 5] Hydrotreating of the heavy oil characterized by carrying out the hydrogen treating of the heavy oil under existence of the catalyst for hydrogen treatings according to claim 1 to 4.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] When this invention is said in more detail about the catalyst for hydrogen treatings of heavy oil, ordinary-pressure residual oil, Impurities and asphaltenes, such as sulfur contents, such as reduced pressure residua oil, an oil sand oil, and a coal liquid, and heavy metal, The hydrogen treating of ****** heavy oil with much carbon residue etc., for example, hydrodesulfurization, High activity is shown also to hydrogenation demetallization, hydrocracking, hydrogenation denitrification, simple hydrogenation (hydrogenation), etc. Upwards, a useful middle cu can be obtained with yield sufficient enough, and there are few sludges and byproductions of Cork. and since a catalyst support is an inflammability, there is also little mixing of the ash content of the catalyst origin, and it does not remove a catalyst for non-decomposed recovered oil (the residual oil which removed the middle cut etc. from the generation oil, and the following -- the same) -- also coming out -- as it is -- a catalyst It is related with the catalyst for hydrogen treatings of heavy oil with the advantage of being able to use it as fuel.
[0002] Namely, the catalyst of this invention can be used suitable for the hydrogen treating of various kinds of heavy oil, and can be especially used in favor of the hydrogen treating of the above ****** heavy oil.
[0003] When this invention is said in more detail about hydrotreating of heavy oil, it relates to the method of performing advantageously the hydrogen treating of various kinds of above-mentioned heavy oil with the application o the catalyst for hydrogen treatings of this invention again.
[0004] In addition, there are fully few an impurity and remains solid contents (Cork, sludge, etc.), such as ****** heavy oil, such as ordinary-pressure residual oil, reduced pressure residual oil, an oil sand oil, and a coal liquid, to a sulfur content and heavy metal, especially, and hydrotreating of this invention is fuel oil (lamp oil, gas oil, etc.), process stock oil, etc. It is applied in favor of the manufacture field of the refining fuel oil (non-decomposed recovered oil) with which the character suitable as various kinds of refining middle-cut products, fuel for boilers, etc. suitable as the good fuel oil of a character, stock oil for FCC processes, etc. has been improved by ****, such as the fractional distillation product as a method of converting into the good hydrocarbon oil which was rich in the suitable middle cut, for example, lamp oil, and gas oil.
[0005]
[Description of the Prior Art] In recent years, importance, such as the hydrogen treating of a hydrocarbon oil, especiall heavy oil, for example, hydrodesulfurization, hydrogenation demetallization, hydrocracking, hydrogenation denitrification, and simple hydrogenation (hydrogenation), is increasing increasingly from the point of earth environment maintenance and a deployment of resources. it -- following -- such a hydrogen-treating reaction -- receiving -- a more effective catalyst -- especially There are many impurities, such as sulfur contents, such as ordinary-pressure residual oil, reduced pressure residual oil, an oil sand oil, and a coal liquid, and heavy metal, sufficient activit is shown to ****** heavy oil with much a part for a part for resin, or an asphaltene and the carbon residue, or super-heavy oil, moreover, there are few sludges and byproductions of Cork and development of a catalyst with the sufficient performance which can obtain efficiently the refined oil which was rich in the useful middle cut by which a sulfur content, heavy metal, etc. were fully reduced is desired.
[0006] As a catalyst for hydrogen treatings, conventionally, according to the purposes, such as a character of target stock oil, and a reaction, a product-quality target, an active-metal kind kind - Combines, and various composition things are used or proposed about the rate of support, the kind of support, the kind of addition component, existence, etc. As the catalyst for hydrogen treatings for performing desulfurization of heavy oil, demetallization, denitrification, decomposition, hydrogenation, etc. also especially in inside Alumina, silica-alumina, and alumina-boria, an alumina-magnesia, To porous inorganic-oxide system support, such as a zeolite, it is a periodic-table VIA group metal

(especially). The catalyst which supported the iron-group metal (Co, nickel, Fe) of Mo, W, and a VIII group with the form of an oxide etc. (For example, CoO-MoO3/aluminum 2O3, NiO-MoO3/aluminum 2O3, NiO-WO3/aluminum 2O3, NiO-CoO-MoO3/aluminum 2O3, etc. are) common. When are accompanied by desulphurization reaction and using a sulfur-content content hydrocarbon oil as a raw material, especially these are usually used, after carrying out reserve sulfidization and being activated.

[0007] If a catalyst is used as the fixed bed in the above heavy oil, especially the hydrogen treating of super-heavy oil, since operation is difficult, it will call at a slurry floor (suspension floor) in many cases by the deposit of Cork. However, when the catalyst which makes support inorganic oxides, such as the above alumina support catalysts, to the slurry floor is used, it is because of ** catalyst being hard. Detailed inorganic substances (ash content), such as;** in which it tends to wear equipment out, consequently a catalyst wear object, arise, since the separation removal is not easy, though a catalyst particle is removed, to the non-decomposed recovered oil after distillation, ash content remains mostly, and there is the trouble; to which the quality is reduced. Although non-decomposed recovered oil is used in many cases as eye a **** hatchet and a home fuel, when non-decomposed recovered oil with much such ash content is burned, there is a problem that the tube wall of a boiler becomes dirty with an inorganic substance.

[0008] In order to solve such a problem, it is thought effective to use what is soft as support of a catalyst inflammable.

[0009] Then, it is possible as support to use the support of organic systems, such as polymer and coal, and coal is [among these] attractive especially from the point of a price.

[0010] As a catalyst for hydrogen treatings which makes coal support, they are lignite (lignite : one sort of brown coal) and bituminous in a U.S. Pat. No. 4,214,977 specification. The catalyst which supported the above active metals to these is proposed using coal (bituminous coal) as support. However, let lignite indicated by this U.S. patent specification, bituminous coal, and the coal more than the level which has degrees of coalification (carbon content), such as an anthracite and semianthracite coal, further be support. When used, to the hydrogen treating of heavy oil, sufficient high activity was not shown and having the fault that there are many byproductions of solid contents, such as Cork and a sludge, made clear especially the catalyst from which an active-metal component is not supported with sufficient rate of high support with sufficient dispersibility, but is obtained.

[0011] Moreover, also in the case of synthetic polymer, generally, it is difficult to support an active-metal component with sufficient dispersibility. The technology which supports an active-metal component with a special method to the rate of high support to special synthetic polymer will be considered, and since a catalyst becomes remarkably expensiv in that case, even if performances, such as activity, are satisfied, as a catalyst for hydrogen treatings of heavy oil, it will be lacking in practicality.

[0012]

[Problem(s) to be Solved by the Invention] this invention is made in view of the above-mentioned situation.

[0013] It is the comparatively soft inflammable support which is cheap as for the first purpose of this invention, and can solve problems, such as the aforementioned wear and mixing of ash content. And the catalyst manufacture conditions for acquiring the hydrogen-treating catalyst of powerful heavy oil easily using the specific support and this specific support which can support an active-metal component with sufficient dispersibility to sufficient rate of support are clarified. Activity high enough can be shown to the hydrogen treating of various kinds of heavy oil, can obtain a useful middle cut with sufficient yield upwards, and There are few byproductions of solid contents (Cork, sludge, etc.), and since inflammable support is moreover used, mixing of ash content decreases remarkably. It is in offering the catalyst for hydrogen treatings of the heavy oil which has the advantage of also being able to use not removing a catalyst for non-decomposed recovered oil suitably as fuel, such as a boiler, with a catalyst as it is.

[0014] this invention also makes it the purpose to offer the method for performing advantageously various kinds of hydrogen treatings of various kinds of heavy oil again fully taking advantage of the advantage using the catalyst for high active hydrogen-ized processing of the above-mentioned this invention.

[0015]

[Means for Solving the Problem] This invention persons thought that the aforementioned purpose could be attained, when the active-metal component could be supported with sufficient dispersibility to flexible inflammable support, and they repeated research wholeheartedly about the matter [what kind or] of composition is suitable as support bearing practicality, such as cost, in mind.

[0016] Consequently, they are degrees of coalification (the rate of the carbon in a dry ash free basis is said.), such as peat and grass peat (peat-moss etc.), also in various kinds of coal. the following -- the same . The following [the existing specific level] found out the outstanding support and the outstanding bird clapper which satisfy the above-mentioned conditions. Furthermore, as a result of advancing research, cellulose system organic substances, such as wood, pulp, a chip, paper, woody fiber, and a vegetable fiber, also became the similarly excellent support, and found

out that it was satisfied also in respect of practicality, such as cost. That is, if such specific coal and a specific cellulose system organic substance were used as support, even if it performed catalyst manufacture by the same conditions and same technique as usual in respect of others, the predetermined active-metal component could be supported with sufficient dispersibility to the rate of high support, and it found out that the highly efficient catalyst for heavy oil hydrogen treatings with which are satisfied of the aforementioned purpose could be acquired easily. In this way, this invention persons succeeded in developing the outstanding catalyst for hydrogen treatings with which are satisfied of the aforementioned purpose which shows the sufficient activity and the sufficient performance for a hydrogen treating of heavy oil of the aforementioned various kinds.

[0017] That is, when the catalyst for hydrogen treatings of this invention prepared in this way, using the aforementioned specific combustible material as support was actually applied to the hydrogen treating of the various heavy oil by the slurry floor etc., it was checked that sufficient hydrogen-treating activity (activity to hydrodesulfurization, hydrogenation demetallization, hydrocracking, etc.) and the yield of a useful middle cut are obtained upwards, and the byproduction of solid contents (Cork, sludge, etc.) is fully reduced. Moreover, compared with the case of the conventional inorganic-oxide support system catalyst, mixing of ash content decreased remarkably from using the flexible inflammable carbonaceous material for support, and decreasing, so that adhesion of the inorganic substance to the tube wall of a boiler etc. can be disregarded, even if it uses the non-decomposed oil collecte without daring remove a catalyst after a reaction as fuel for a boiler with the catalyst was also checked.

[0018] This invention persons came to complete this invention based on the above-mentioned knowledge.

[0019] That is, this invention offers the catalyst for hydrogen treatings of the heavy oil to which the rate of the carbon in a dry ash free basis supports the compound of a periodic-table VIA group metal, and/or the compound of a periodic-table VIII group's iron-group metal at least to the coal or the cellulose system organic substance which is 65 or less % of the weight, and is characterized by the bird clapper.

[0020] Moreover, this invention offers collectively hydrotreating of the heavy oil characterized by carrying out the hydrogen treating of the heavy oil under existence of this catalyst for hydrogen treatings as an example of application of the catalyst for hydrogen treatings of the above-mentioned this invention.

[0021] A. The catalyst for hydrogen treatings and the catalyst for hydrogen treatings of the manufacture this invention are prepared using the combustible material (it may be hereafter called coal [I] that this specific coal should be distinguished from other general coal) of the aforementioned specification, i.e., the coal whose rate of the carbon in a dry ash free basis is 65 or less % of the weight, or a cellulose system organic substance as support.

[0022] Although what thing or application is possible if the rates of the carbon in a dry ash free basis are coal which is 65 or less % of the weight as the aforementioned coal [I] which it faces preparing the catalyst for hydrogen treatings of this invention, and is used as support, peat and grass peat (for example, peat-moss etc.) can be especially mentioned as a desirable thing. The coal [I] of these various kinds may use only one sort, and it may use together two or more sorts of things as mixture etc. according to a case.

[0023] If high coal, for example, an anthracite, semianthracite coal, bituminous coal, a subbituminous coal, a general lignite, brown coal of a degree of coalification with the larger rate of the carbon in a dry ash free basis than 65 % of the weight, etc. are made into support, since it is difficult to support the aforementioned predetermined active-metal component with a good support state here, it is difficult to acquire the catalyst of the request which has the activity and the performance sufficient by the support technique general at least conventionally for the hydrogen treating of ****** heavy oil. In addition, even if satisfied with the hydrogen-treating catalyst which such a degree of coalification prepared by the conventional method by making general high coal into support in respect of activity and the yield of a middle cut, the byproduction of remains solid contents (Cork, sludge, etc.) increases, and the purpose of this invention cannot be attained. The desirable rate of the carbon in a dry ash free basis is 30 - 65 % of the weight more preferably ten to 65% of the weight.

[0024] It faces preparing the catalyst of this invention and various kinds of cellulose system organic substances are usable as support. As this cellulose system organic substance, for example, wood, paper, pulp, a chip, woody fiber, a vegetable fiber, etc. can be mentioned, and pulp, a chip, paper, etc. are desirable also in especially inside.

[0025] As for wood, what is obtained from various kinds of portions (a stalk, a branch, bark, etc.) of various kinds of bolts, such as a needle-leaf tree, a broad-leaved tree, or plants, is usable here. these If processed into suitable size and configuration, a green-wood-like thing, a dead tree-like thing, To these, or for example, dryness, humidity, warm water or hot water processing, steam processing, It can be suitably used with various kinds of forms, such as chemical [various] or various things which performed physical processing, such as processing of washing, extraction, etc. by acid treatment, base processing, halogenation processing, sulfurous-acid (salt) processing, the alkali-metal salt water solution, the organic solvent, etc., partial oxidation processing, a hydrogen treating, sulfidization, and dry distillation.

Of course, you may use what was processed into the plywood etc., for example, the recovery material after use, the edge material which carries out a byproduction at a processing process, sawdust, scrap wood, etc.
[0026] Moreover, the same is said of paper or pulp and the thing of various kinds of forms acquired from various kinds of raw materials is usable. If it consists of cellulose nature fiber speaking of paper, what thing is sufficient as western paper, Japanese paper, semisynthesis paper, a synthetic paper, compound paper, etc., for example, its ********, such as the thing or toilet paper objects for building materials, such as a thing for the usual printing, a thing for packing, shoji paper, and wallpaper, or for designs, and tissue, are also usable. Moreover, you may use suitably the kudzu paper which carried out the byproduction by used paper, recycled paper, cutting, etc. from the point of economical efficiency Also in such papers of various kinds of, that into which support liquid, such as toilet paper and tissue, tends [especially] to sink is used suitably. The pulp of both dissolving pulp and paper pulp is also usable.
[0027] Sawmill scrap wood etc. can be mentioned as the aforementioned chip.
[0028] The fiber of the cellulose nature obtained from various kinds of trees, wood, pulp, paper, etc. as the aforementioned woody fiber or a fiber bundle, a blanket-like thing, etc. can be mentioned.
[0029] Moreover, the natural fiber which used various kinds of vegetation as the raw material as the aforementioned vegetable fiber, or its workpiece (thread and cloth may be used) is usable, for example, can mention various kinds of things, such as a thing of the system of others, such as vein fiber, such as bast fibers, such as seed fibers, such as cotton a kapok, and a panja, a kozo, Mitsu Mata, flax, and a jute, and hemp, or a coconut, straw, a spiral spring, and ** ZURU.
[0030] In addition, each may be independently used for the aforementioned wood, paper, pulp, a chip, woody fiber, a vegetable fiber, etc. as support, and they can also use two or more sorts together as mixture or a composite.
[0031] By the way, the coal [I] and the cellulose system organic substance which are used as the aforementioned support are suitably used as various kinds of sizes or a thing of a configuration so that it may be easy to support an active-metal component at least at the time of catalyst manufacture. Of course, in that case, you may use by making it predetermined size and configuration beforehand so that the reaction method to be used may be suited.
[0032] For example, although speaking of coal [I] you may use as it is, of course as long as size and a configuration are suitable, you may use by making it suitable size and a suitable configuration by the classification etc. a pulverization, decision, and screen exception if needed, or what gave a granulation and fabrication may be used suitably. In using it for a slurry floor, it becomes suitable [what was only ground in the shape of fines with the ball mill etc.].
[0033] Moreover, what is necessary is for the same to be said of a cellulose system organic substance, for example, just to use it for suitable size and configurations, such as the shape of sawdust, and a letter of a chip, in the case of wood, carrying out. What is necessary is to cut suitably in the shape of [of a suitable size and configuration] a chip, or to unfold, or just to use it also about paper, pulp, woody fiber, and a vegetable fiber, fabricating and processing it.
[0034] In addition, after performing various kinds of chemical preparation and physical processings which were indicated to the explanation about the aforementioned wood prior to support according to a case, you may use the aforementioned coal [I] and a cellulose system organic substance. However, when advancing carbonization by dry distillation etc., in any case, it is required to control a degree of coalification so that the rate of the carbon in a dry ash free basis becomes 65 or less % of the weight of a range.
[0035] The catalyst for hydrogen treatings of this invention is prepared by supporting the compound of a periodic-table VIA group metal, and/or the compound of a periodic-table VIII group's iron-group metal at least to this support, using one sort in various kinds of aforementioned coal [I] and a cellulose system organic substance, or two sorts or more as support. Thus, as long as the aforementioned coal [I] and a cellulose system organic substance are used as support, the rest may support the aforementioned predetermined active-metal component according to a conventional method.
[0036] In addition, on these specifications, the VIA group metal and the iron-group metal are called active metal timely.
[0037] As the aforementioned VIA group metal, here where molybdenum, a tungsten, and chromium are mentioned is made, and molybdenum and a tungsten are usually desirable also in these. On the other hand, iron, cobalt, and nickel can be mentioned as the aforementioned iron-group metal. What metal kind is supported among these VIA(s) group metal and an iron-group metal should just select it suitably as usual according to a case.
[0038] generally, it is desirable to combine suitably one sort or two sorts or more of VIA group metal kinds, one sort, or two sorts or more of iron-group metal kinds, and to use them in consideration of the metaled combination effect, and especially, although combination, such as nickel-Mo, nickel-W, Co-Mo, Co-W, nickel-Mo-W, nickel-Co-Mo, Fe-Mo, and Fe-W, is desirable, it is not necessarily limited to these
[0039] Depending on the case, only one sort or two sorts or more of VIA group metal kinds may be supported, or only one sort or two sorts or more of iron-group metal kinds may be supported. Furthermore, in any case, you may add other

metal kinds other than a VIA group metal and an iron-group metal etc. suitably if needed. In addition, in supporting only an iron-group metal kind, it usually becomes suitable [the combination of nickel independence or nickel-Co, nickel-Fe, and nickel-Fe-Co] preferably from the point of activity to use nickel at least as a support metal kind in this case. Moreover, in supporting only a VIA group metal kind, it usually becomes suitable [the combination of Mo independence or Mo-W, Mo-Cr, and Mo-W-Cr] preferably as a support metal kind in this case to use Mo at least.
[0040] The suitable amount of support of the aforementioned active-metal component in the catalyst for hydrogen treatings of this invention Since it changes with the kind and form of the carbonaceous material used as support, the kind of metal to support, the character of the heavy oil which combines or carries out a hydrogen treating again, purposes of a process, etc. Although it cannot set uniformly, it usually calculates by weight % of the metal of per a catalyst weight (weight of the catalyst after support dryness). a VIA group metal (total quantity) -- 0.5 - 30% of the weight of the range -- and selecting so that an iron-group metal (total quantity) may become 1 - 50% of the weight of a range -- desirable -- especially -- the former -- 2 - 15% of the weight of the range -- and it is more desirable to select the latter in 2 - 20% of the weight of the range Here, the amount of support of a VIA group metal may be less than 0.5 % of the weight, or if the amount of support of an iron-group metal is less than 1 % of the weight, sufficient hydrogen-treating activity may not be obtained. On the other hand, even if it makes the amount of support of a VIA group metal larger than 30 % of the weight or makes the amount of support of an iron-group metal larger than 50 % of the weight, the improvement in the activity beyond it is not found, but the trouble of activity falling may be produced on the contrary.
[0041] In addition, although it is desirable to select each in the same range as the above when supporting only iron-group metals, such as a case where only VIA group metals, such as Mo, are supported, and nickel, as described above, generally the activity tends to become low as compared with the case where a VIA group metal and an iron-group metal are selected and supported in the above-mentioned range.
[0042] It faces supporting the active-metal kind (a VIA group metal and/or iron-group metal) selected as mentioned above to the aforementioned predetermined support, and these active metals are used as gestalten, such as solution of a suitable compound, respectively. There is especially no limit also as the support technique in that case, and various kinds of support methods can be applied so that it may mention later.
[0043] That is, it faces preparing the support liquid used in case an active-metal compound is supported to the aforementioned support, and the aforementioned active metal can be used as a variety of compounds. Although it has usually taken the gestalt of solution, since this support liquid adds a suitable additive according to a case like the after-mentioned, and it can raise the solution nature of the active-metal compound or it can raise the stability of a solution or the occasion of manufacture of this support liquid, the active-metal compound to be used may not necessarily have water-soluble itself. In short, as an active-metal compound used as a manufacture raw material, although it is desirable to present support in the state where it was made to dissolve as uniformly as possible as for an active-metal kind, if such conditions are fulfilled as a result, it can apply the thing of any kinds and a gestalt.
[0044] Manufacture of support liquid is faced. the aforementioned VIA group metal for example, an oxide (MoO_3, WO_3, CrO_3 grade), a hydroxide, or an oxygen acid (a molybdic acid --) Oxygen-acid salts, such as a tungstic acid, a heteropolyacid, and chromium hydroxide for example, an ammonium molybdate and tungstic-acid ammonium -- Halogenides, such as a heteropolyacid salt and an ammonium chromate, or an oxy-halogenide for example, $MoCl_5$, $MoOCl_3$, WCl_6, $WOCl_4$, and WO -- 2 Cl $CrCl_3$, CrO_2Cl_2 grade, a sulfide (for example, MoS_2, WS_2 grade), complex [, such as these **, such as organic acid chloride, such as a cyanide, a nitrate [$Cr(NO_3)_3$ grade], a sulfate [$Cr_2(SO_4)_3$ grade], and acetate, and an alkoxide, -- for example One sort or two sorts or more can be used as a thing of various kinc and gestalten, such as a thing of colloid gestalten, such as **] and also hydrogels, such as an EDTA complex, an acetylacetonato complex, a nitrosyl complex, and a carbonyl complex, and a sol-like compound.
[0045] Also in these, about Mo and W, usually, oxygen-acid salts, such as oxygen acids, such as an oxide of MoO_3 or WO_3 grade, a molybdic acid, and a tungstic acid, a paramolybdate, a metamolybdate, parawolframate, and a metatungstate, etc. are used suitably, and a paramolybdate, a metamolybdate, parawolframate, a metatungstate, etc. are used especially suitably. In addition, there are various kinds of salts, such as an ammonium salt and an alkali salt, and although each of these is usable, an ammonium salt is usually especially used for these molybdates and a tungstate suitably.
[0046] in addition, although the solubility to water is [that it is not so large and] also in these Mo and oxides of W, oxygen acids, or an oxygen-acid salt if it remains as it is, a suitably suitable additive, for example, an organic acid, EDTA, etc. are added also about such a thing, or pH of liquid can be adjusted and solubility and dissolution stability can be raised
[0047] On the other hand, the aforementioned iron-group metal can also be used as a variety of compounds on the

occasion of manufacture of support liquid. specifically for example For example, halogenides, such as a nitrate, a carbonate, a basic carbonate, a sulfate, and a chloride, Organic acid chloride, such as mineral salt, such as a sulfide and a cyanide, acetate, a tartrate, and a benzoate, Further an oxide, a hydroxide, an alkoxide, etc. Complexes, such as such complex salt An ammine complex, an aquo complex, an EDTA complex, an acetylacetonato complex, a carbonyl complex, halogen acid, or a halogen acid salt for example, further One sort or two sorts or more can be used as a thing of various kind and gestalten, such as a thing of colloid gestalten, such as a hydrogel, and a sol-like compound, metal colloid.

[0048] In addition, also in these, about cobalt and nickel, a nitrate, a carbonate, a basic carbonate, etc. are usually desirable, and a nitrate etc. is usually desirable about iron.

[0049] The catalyst for hydrogen treatings of this invention can be prepared by the same technique as usual about other points, as long as the aforementioned predetermined active-metal compound is supported to the aforementioned predetermined support. However, it is better to avoid baking by the gas which contains after support comparatively many oxygen, such as air in an elevated temperature which is usually carried out, since the inflammable matter was used as support in the case of this catalyst for hydrogen treatings. In other words, in the case of this catalyst, although it calcinates and drops off at such an elevated temperature, hydrogen-treating activity comparatively sufficient by dryness processing at low temperature is obtained so that it may mention later.

[0050] Support of the active-metal compound to the aforementioned support can be suitably performed according to various kinds of well-known support operation technique, such as various kinds of sinking-in methods (a vacuum impregnation method, the heating sinking-in method, etc.), dip coating, the kneading method, and a spray method.

[0051] In addition, as described above, you may perform the aforementioned support under coexistence of a suitable addition component suitably if needed. For example, in order to support more uniformly and stably by being a support way or raising further the stability of the solution of the active-metal compound with which support is presented, adding suitable organic acids, such as a carboxylic acid, is adopted suitably.

[0052] In this case, oxalic acid, a tartaric acid, a succinic acid, a malonic acid, a malic acid, a citric acid, formic acid, an acetic acid, a propionic acid, etc. can specifically [as an organic acid, various kinds of things are usable, and] be illustrated. these organic acids -- the need -- responding -- one sort -- or two or more sorts may add

[0053] In that case, as for the rate of the organic acid to add, it is desirable to select in the range of the 0.1 - 100 weight section as opposed to the dry weight 100 weight section of the support to be used, and it is desirable to select in the range of 5 - 50 weight section especially. when the addition effect of an organic acid is not demonstrated by ten parts as it is under the 0.1 weight section on the criteria of the above [this rate], but the 100 weight sections are exceeded on the other hand, the bird clapper has supported difficult rather uniformly for the reasons of the solubility of an active-metal compound becoming bad

[0054] The catalyst for hydrogen treatings of this invention can be suitably acquired by drying, after supporting a predetermined active-metal compound as mentioned above.

[0055] As this drying temperature, it is usually suitable preferably to select [50-150-degree C] in the range of 80-120 degrees C. This dryness is usually suitably carried out in air atmosphere. Or support burns and is anxious even if it dries in air if it is such a temperature requirement, in many cases, it is because the active-metal compound in the inside of this air which supported at least dryness is fully activable to active species again. In addition, this dryness may not necessarily be performed in air atmosphere, either, and depending on the kind of used active-metal compound, sufficient activation is made by reduced pressure drying or dryness in an inert gas air current, and it may perform dryness and activation in reducing gas, such as hydrogen, or other suitable gas atmosphere according to a case, for example.

[0056] Moreover, after dryness, suitably, it may process by inert gas, such as nitrogen, or you may calcinate by the gas of a suitable oxygen density in the range in which it is suitable temperature, for example, support does not burn, and hydrogen, a hydrogen sulfide, or its mixed gas may perform activation, such as reduction or preliminary sulfuration, further if needed.

[0057] In this way, the catalyst for hydrogen treatings of the prepared this invention As opposed to the hydrogen treating of various kinds of heavy oil, especially heavy oil (super-heavy oil etc.) of **** which was described above Since have sufficient activity, the yield of sufficient useful middle cut is given upwards, remains solid-content byproductions, such as Cork and a sludge, have the catalyst performance which was [be / few / it] excellent and the flexible inflammable matter is moreover used for support Even if it uses for a slurry floor, there is no problem of wear of equipment, and mixing of the ash content to a generation oil or its distillation residue (non-decomposed recovered oil) also decreases remarkably. Therefore, it has the various advantages of not removing a catalyst also being able to use non-decomposed recovered oil etc. suitably as fuel for boilers etc. as it is.

[0058] Although the catalyst for hydrogen treatings of the aforementioned this invention turns into a catalyst not necessarily effective not only in the hydrogen treating of heavy oil but the hydrogen treating of other general targets' more ****** sulfur-containing hydrocarbon oil, since it can be effectively used especially to heavy oil and the hydrogen treating of super-heavy oil, it has been called the catalyst for hydrogen treatings of heavy oil.
[0059] Below, hydrotreating of the heavy oil of this invention which is the example of application of the catalyst for hydrogen treatings of this invention is explained.
[0060] B. Hydrotreating of the heavy oil of the hydrotreating this invention of heavy oil is characterized by performing the hydrogen treating of heavy oil, for example, hydrodesulfurization, hydrogenation demetallization, hydrocracking, hydrogenation denitrification, simple hydrogenation (hydrogenation), etc. using the catalyst for hydrogen treatings of the aforementioned this invention at least.
[0061] By the way, although there were various things in the catalyst for hydrogen treatings of this invention by composition of a catalyst, the difference among manufacture conditions, etc. as described above, the coal [I] used as support or the kind of cellulose system organic substance, the kind of active metal, combination, the rate of support, etc. already explained from each point what catalyst is [among these] desirable. Of course, which catalyst is actually used selects a suitably best thing according to a case, and it should just be used for it. Which catalyst serves as best For example, the character of the heavy oil used as a raw material, Especially Reaction methods, such as a sulfur content, a boiling range, or the degree of heavy, a reaction condition, Since it changes with how far the purpose of a process, for example, a sulfur content, is reduced or hydrocracking are aimed at the thing of what boiling range, advancing how many hydrocracking and using it as a middle cut, and terms and conditions It is good, if a preliminary test is performed and best selects suitably in consideration of such conditions if needed.
[0062] That is, in the method of this invention, under existence of at least one sort of catalysts selected from the catalysts for hydrogen treatings of various kinds of aforementioned this inventions, heavy oil is contacted to hydrogen gas on suitable conditions, and a hydrogen treating is performed.
[0063] In that case, the catalyst of this invention may be used independently and may use two or more sorts together.
[0064] As heavy oil used as stock oil, although oil sand oils, such as ordinary-pressure residual oil, reduced pressure residual oil, etc. which are obtained by various kinds of atmospheric distillation and vacuum distillation of a crude oil, coal liquid, etc. can be mentioned, it is not necessarily limited to these, for example. In addition, according to a case, the heavy oil from which two or more sorts of characters differ may be mixed, or a ****** hydrocarbon fraction may be mixed by heavy oil, and you may use as stock oil.
[0065] It is usually suitable for the reaction temperature of the aforementioned hydrogen treating preferably to select [300-550-degree C] in the range of 350-500 degrees C. It is usually suitable 20-200 kg/cm2G and to select the hydrogen pressure force in the range of 50-150 kg/cm2G preferably.
[0066] Although there is especially no limit, for example, all can apply the fixed bed, the moving bed, a suspension floor (slurry floor), an ebullating bed, etc. as a reaction type formula, a suspension floor is especially adopted suitably from points, such as thermal efficiency and operability. In addition, although it is good also by the batch process or the half-batch process in the case of a suspension floor, points, such as productivity, to a flow method is usually desirable.
[0067] In the case of such a flow method, it is usually good 0.05-5h-1 and to select supply liquid space velocity (LHSV) in the range of 0.2-2h-1 preferably.
[0068] It is usually suitable 50-1000Nm3/kl and to select preferably the supply rate (H2 / raw material heavy oil) of hydrogen gas and raw material heavy oil in the range of 100-800Nm3/kl.
[0069] The hydrogen treating of various kinds of above-mentioned heavy oil can be performed suitably as mentioned above, there are fully few impurity contents for heavy metal, such as a sulfur content and nitrogen content, etc., and they can be efficiently converted into the good hydrocarbon oil of the character which was rich in the useful middle cut Moreover, according to this method, various advantages using the catalyst for hydrogen treatings of this invention which was described above (highly efficient catalyst which carries out support of the combustible material) -- there is no mixing of the ash content to the inside of a generation oil with few byproductions of a remains solid content -- are demonstrated.
[0070] That is, not separating a catalyst can also use suitably the generation oil (reaction mixture) obtained in this way as fuel oil etc. Of course, you may separate and use a catalyst like a conventional method. since it is convenient even if the detailed catalyst which is hard to separate remains when separating a catalyst such, there is an advantage, like easy separation operation also comes out enough and there is
[0071] Moreover, although the obtained generation oil is usually divided into various kinds of desired fractions according to conventional methods, such as distillation, and it is used for each purpose Also in this case, although the remains solid contents (Cork, sludge, etc.) of a catalyst and a some are contained in the residual oil at the time of darin

separate a catalyst, and also dropping off, for example, distillation etc. separating comparatively ****** fractions, such as a middle cut, (non-decomposed recovered oil) This non-decomposed recovered oil can be suitably used as fuel for boilers, even if it remains as it is. Of course, you may remove a catalyst or a catalyst, and remains solid contents (Cork, sludge, etc.) suitably in one of stages also in this case.

[0072] the middle cut distillled fractionally in this way on the other hand -- large -- the fraction about naphtha - gas oil - lamp oil and a gas oil fraction can usually be made into a principal component, for example, it can use effectively as the stock oil for processes, such as an FCC process, or good fuel oil of a character

[0073]

[Example] Although the example and its example of comparison of this invention are shown below and these still more specifically explain this invention to it, this invention is not limited to these examples.

[0074] Example 1 ammonium molybdate [(NH4)6Mo7O24.4H2O] 2.63g, nickel nitrate [nickel(NO3)3]2.64g, and malic-acid [HOOCCH(OH) CH2COOH]1.5g were dissolved in ion exchange water, the whole quantity was prepared t 45ml, and sinking-in liquid was prepared.

[0075] The aforementioned sinking-in liquid was added to 23.8g (60.2 % of the weight of degrees of coalification) (dry weight of 15g) of peat sifted out to 1mm or less, moisture was evaporated, agitating on the sand bath heated at 200 degrees C, and the predetermined active-metal component etc. was supported.

[0076] Subsequently, the obtained support object was ground after 12-hour dryness for 1 hour using the ball mill at 12(degrees C.

[0077] In this way, the mean particle diameter of the acquired catalyst is about 1 micrometer, and contained 3 % of the weight of nickel, and 8 % of the weight of molybdenum as a metal per dry weight.

[0078] It taught auto KUREGU with a capacity of 300ml with 80g (ARABIAN heavy reduced pressure residual oil) of stock oil of the character which shows 0.81g of this catalyst in Table 1, the reaction was performed under 450 degrees C and the hydrogen pressurization of 130 kg/cm2G for 1 hour, and activity, a performance, etc. as a hydrogen-treating catalyst were evaluated. This evaluation result is shown in Table 2 with other examples and the example of comparison

[0079] Except having used 24.0g (54.7 % of the weight of degrees of coalification [Peat-moss :]) (dry weight of 15g) of grass peat instead of peat in example 2 example 1, the catalyst was prepared similarly and the activity and performance were also evaluated similarly. A result is shown in Table 2.

[0080] Except having used 16.9g (44 % of the weight of carbon contents [Toilet paper :] per dry weight) (dry weight of 15g) of papers instead of peat in example 3 example 1, the catalyst was prepared similarly and the activity and performance were also evaluated similarly. A result is shown in Table 2.

[0081] Except having used 17.9g (68.4 % of the weight of degrees of coalification) (dry weight of 15g) of brown coal instead of peat in example of comparison 1 example 1, the catalyst was prepared similarly and the activity, performance, etc. were evaluated similarly. A result is shown in Table 2.

[0082] Except having used 15g (82.7 % of the weight of degrees of coalification) of bituminous coal instead of peat in example of comparison 2 example 1, the catalyst was prepared similarly and the activity, performance, etc. were evaluated similarly. A result is shown in Table 2.

[0083]

[Table 1]

性状 ＼ 原料油		アラビアンヘビー減圧残油 (VR－AH)
比重 (15／4℃)		1．0130
動粘度（cSt） @100℃		1770
硫黄分（wt%）		5．03
窒素分（wt%）		0．312
金属分（ppm）	バナジウム	115
	ニッケル	36
残留炭素（wt%）		21．6
全水素分（wt%）		10．0
アスファルテン分（wt%）		11．3

[0084]
[Table 2]

		実施例			比較例	
		1	2	3	1	2
担体		泥炭	草炭 (ピートモス)	紙	褐炭	瀝青炭
元素分析 wt%	炭素	60.2	54.7	44.4	68.4	82.7
	水素	5.2	5.4	6.2	4.7	4.7
	窒素	2.5	1.4	0.0	0.5	0.9
	硫黄	0.4	0.3	0.0	0.1	0.9
	酸素	31.8	38.2	49.4	26.3	10.8
	(全て、無水無灰ベースでの値)					
反応成績	中間留分 wt% (174－343℃)	28.3	28.3	28.6	28.5	27.7
	固形分収率 wt% (ヘプタン不溶分)	12.1	9.3	12.2	14.3	20.4
	525℃以下の留分への転化率 wt%	76.5	76.5	76.9	76.2	72.8

[0085] If cellulose system organic substances, such as low coal of degrees of coalification, such as peat and grass peat (peat-moss), and paper, are used as support so that it may understand also from the <consideration of result> table 2, reaction results will improve compared with the case where the high coal of a degree of coalification is used. Even if especially the ratio of a middle cut is of the same grade, the yield of solid contents (Cork, sludge, etc.) is fully reduced.
[0086]
[Effect of the Invention] It is supple with an inflammability called low coal and a cellulose system organic substance in a degree of coalification, and the catalyst for hydrogen treatings of this invention is sufficient rate of high support abou a cheap active-metal component predetermined moreover. Since it is prepared using specific support with the property with the ability to support [sufficient] with sufficient dispersibility, sufficient activity and a sufficient performance are demonstrated upwards to the hydrogen treating of various kinds of heavy oil, and it has the various advantages based on the inflammability of support, flexibility, etc. When saying concretely and the catalyst of this invention is used for heavy oil or the hydrogen treating of super-heavy oil. The yield of (i) useful middle cut and the hydrogen-treating activity as the whole come out enough. for example, to a certain top The problem of the wear of equipment which had become with the problem in the case of the catalyst for hydrogen treatings of the conventional inorganic-oxide support system is solved, and especially, since mixing of ash content is lost even if it obtains with catalysts and atomizes When not daring carry out separation removal of the catalyst can also use non-decomposed recovered oil suitably as fuel for boilers as it is and it separates a catalyst, it is; easy [operation] and good.
(ii) Let the high coal of a degree of coalification called the lignite (lignite) and bituminous coal of which the conventional proposal is done be support. Although it is good almost similarly [the same conditions compare and] about the yield of a middle cut compared with the case of the catalyst for hydrogen treatings used and prepared, the activity as the whole increases in many cases, and the effect excellent in; to which the byproduction of a remains solid content decreases sharply especially is demonstrated.
[0087] Moreover, since the hydrogen treating of the heavy oil of this invention becomes advantageous [in respect of the above (i) and (ii)] at least as compared with the case where the conventional catalyst for hydrogen treatings is used since the catalyst for highly efficient hydrogen treatings of the above-mentioned this invention is used, the industrial value is very large.

[Translation done.]

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(54)【発明の名称】　重質油の水素化処理用触媒及びそれを用いる重質油の水素化処理法

(57)【要約】

【目的】　柔らかくかつ可燃性の物質を担体として用い、これに水素化活性を有する金属成分を分散性よく担持させ、重質油の水素化処理に用いた場合に十分な水素化活性を有し、さらに未分解回収油を、触媒を除去しないでもそのまま触媒と共に燃料として使用することができる水素化処理用触媒を提供する。この水素化処理用触媒を用いて重質油の各種水素化処理を有利に行うための方法を提供する。

【構成】　無水無灰ベースでの炭素の割合が６５重量％以下である石炭又はセルロース系有機物質に、少なくとも周期表ＶＩＡ族金属の化合物及び／又は周期表ＶＩＩＩ族の鉄属金属の化合物を担持してなることを特徴とする重質油の水素化処理用触媒、ならびに、この水素化処理用触媒の存在下で重質油を水素化処理する重質油の水素化処理法。

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【特許請求の範囲】

【請求項1】　無水無灰ベースでの炭素の割合が65重量%以下である石炭又はセルロース系有機物質に、少なくとも周期表ＶＩＡ族金属の化合物及び／又は周期表ＶＩＩＩ族の鉄族金属の化合物を担持してなることを特徴とする重質油の水素化処理用触媒。

【請求項2】　前記石炭が泥炭又は草炭である請求項1に記載の水素化処理用触媒。

【請求項3】　前記セルロース系有機物質が、木材、パルプ、チップ、紙、木質繊維又は植物繊維である請求項1に記載の水素化処理用触媒。

【請求項4】　前記セルロース系有機物質が、パルプ、チップ又は紙である請求項1又は3に記載の水素化処理用触媒。

【請求項5】　請求項1～4のいずれかに記載の水素化処理用触媒の存在下で重質油を水素化処理することを特徴とする重質油の水素化処理法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、重質油の水素化処理用触媒に関し、より詳しく言うと、常圧残油、減圧残油、オイルサンド油、石炭液化油等の、硫黄分、重金属等の不純物やアスファルテン、残留炭素分等の多い劣質な重質油の水素化処理、例えば水素化脱硫、水素化脱金属、水素化分解、水素化脱窒素、単純水素化（水添）等に対しても高い活性を示し、有用中間留分を十分に収率よく得ることができる上に、スラッジ、コークの副生が少なく、しかも、触媒担体が可燃性であるので触媒由来の灰分の混入も少なく、未分解回収油（生成油から中間留分等を除去した残油、以下同様）を、触媒を除去しないでもそのまま触媒と共に燃料として使用することができるなどの利点を有す重質油の水素化処理用触媒に関する。

【0002】すなわち、本発明の触媒は、各種の重質油の水素化処理に好適に使用することができ、特に、上記のような劣質な重質油の水素化処理に有利に利用することができる。

【0003】本発明は、また、重質油の水素化処理法に関し、より詳しく言うと、上記の各種の重質油の水素化処理を、本発明の水素化処理用触媒を適用して有利に行う方法に関する。

【0004】なお、本発明の水素化処理法は、特に、常圧残油、減圧残油、オイルサンド油、石炭液化油等の劣質な重質油から、硫黄分や重金属等の不純物や残留固形分（コーク、スラッジ等）が十分に少なく、燃料油（灯油、軽油等）やプロセス原料油等として好適な中間留分に富んだ良質な炭化水素油に転化する方法として、また、その分留製品、例えば、灯油、軽油等の軽質で性状のよい燃料油やＦＣＣプロセス用原料油等として好適な各種の精製中間留分製品とボイラー用燃料等として好適な性状が改善された精製重油（未分解回収油）の製造分野に有利に適用される。

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【0005】

【従来の技術】近年、地球環境保全及び資源の有効利用の点から、炭化水素油、特に重質油の水素化処理、例えば水素化脱硫、水素化脱金属、水素化分解、水素化脱窒素、単純水素化（水添）等の重要性がますます増加している。それに伴い、こうした水素化処理反応に対してより有効な触媒、特に、常圧残油、減圧残油、オイルサンド油、石炭液化油等の硫黄分や重金属類等の不純物が多く、レジン分やアスファルテン分更には残留炭素分の多い劣質な重質油、若しくは超重質油に対して十分な活性を示し、しかもスラッジやコークの副生が少なく、硫黄分、重金属等が十分に低減された有用中間留分に富んだ精製油を効率よく得ることができる性能のよい触媒の開発が望まれている。

【0006】水素化処理用触媒としては、従来、対象とする原料油の性状や反応、製品品質目標等の目的に応じて、活性金属種の種類・組み合わせ、その担持率、担体の種類、添加成分の種類や有無などについて多種多様な組成ものが使用若しくは提案されている。中でも特に、重質油の脱硫、脱金属、脱窒素、分解、水添などを行うための水素化処理用触媒としては、アルミナ、シリカーアルミナ、アルミナーボリア、アルミナ－マグネシア、ゼオライト等の多孔性無機酸化物系担体に、周期表ＶＩＡ族金属（特に、Ｍｏ、Ｗ）とＶＩＩＩ族の鉄族金属（Ｃｏ、Ｎｉ、Ｆｅ）を酸化物等の形態で担持した触媒（例えば、$CoO \cdot MoO_3/Al_2O_3$、$NiO \cdot MoO_3/Al_2O_3$、$NiO \cdot WO_3/Al_2O_3$、$NiO \cdot CoO \cdot MoO_3/Al_2O_3$など）が一般的であり、これらは、特に脱硫反応を伴う場合など硫黄分含有炭化水素油を原料とする場合には、通常、予備硫化処理し活性化した後に使用されている。

【0007】上記のような重質油、特に超重質油の水素化処理にあたっては、触媒を固定床として用いるとコークの析出により運転が難しいので、スラリー床（懸濁床）によることが多い。ところが、スラリー床で上記のようなアルミナ担持触媒等の無機酸化物を担体とする触媒を用いると、①触媒が固いため、装置が摩耗しやすい；②その結果、触媒摩耗物等の微細な無機物（灰分）が生じ、その分離除去が容易でないため、触媒粒子を除去したとしても蒸留後の未分解回収油には灰分が多く残留し、その品質を低下させる；といった問題点がある。未分解回収油は劣質なため、自家燃料として使用することが多いが、そのような灰分の多い未分解回収油を燃焼させるとボイラーの管壁が無機物で汚れるという問題がある。

【0008】このような問題を解決するには、触媒の担体として柔らかく可燃性のものを用いることが有効と思われる。

【0009】そこで、担体として、例えば、ポリマー、

石炭等の有機系の担体を用いることが考えられ、これらのうち、価格の点からは特に石炭が魅力的である。

【００１０】石炭を担体とする水素化処理用触媒として、米国特許第４，２１４，９７７号明細書には、ｌｉｇｎｉｔｅ（亜炭：褐炭の１種）やｂｉｔｕｍｉｎｏｕｓ　ｃｏａｌ（瀝青炭）を担体として用い、これらに上記のような活性金属類を担持した触媒が提案されている。しかしながら、該米国特許明細書に記載されているｌｉｇｎｉｔｅや瀝青炭、更には無煙炭、半無煙炭等の炭化度（炭素含量）があるレベル以上の石炭を担体として用いると、活性金属成分が十分な高担持率で分散性よく担持されず、得られる触媒は、重質油の水素化処理に対して十分な高活性を示さなかったり、特に、コーク、スラッジ等の固形分の副生が多いという欠点を有することが判明した。

【００１１】また、合成ポリマーの場合にも、一般に、活性金属成分を分散性よく担持することは困難である。特殊な合成ポリマーに特殊な方法で活性金属成分を高担持率まで担持する技術も考えられるが、その場合には触媒が著しく高価になるのでたとえ活性等の性能が満足されたとしても重質油の水素化処理用触媒としては実用性に乏しい。

【００１２】

【発明が解決しようとする課題】本発明は、上記の事情に鑑みてなされたものである。

【００１３】本発明の第一の目的は、安価で前記摩耗や灰分の混入等の問題を解決することができる比較的柔らかく可燃性の担体であって、しかも活性金属成分を十分な担持率まで分散性よく担持することができる特定の担体及び該担体を用いて性能の良い重質油の水素化処理触媒を容易に得るための触媒調製条件を明らかにし、各種の重質油の水素化処理に対して十分に高い活性を示し、有用中間留分を収率よく得ることができる上に、固形分（コークやスラッジ等）の副生が少なく、しかも可燃性の担体を用いていることから灰分の混入が著しく少なくなり、未分解回収油を、触媒を除去しないでもそのまま触媒と共にボイラー等の燃料として好適に使用することができるなどの利点を有する重質油の水素化処理用触媒を提供することにある。

【００１４】本発明は、また、上記本発明の高活性水素化処理用触媒を用いて、その利点を十分に活かし、各種の重質油の各種の水素化処理を有利に行うための方法を提供することも目的としている。

【００１５】

【課題を解決するための手段】本発明者らは、柔軟で可燃性の担体に活性金属成分を分散性よく担持することができれば前記目的を達成できると考え、どのような種類あるいは組成の物質が担体として適切かどうかについて、コスト等の実用性をも念頭において鋭意研究を重ねた。

【００１６】その結果、各種の石炭類の中でも泥炭や草炭（ピートモスなど）等の炭化度（無水無灰ベースでの炭素の割合をいう。以下同様。）がある特定のレベル以下のものが、上記の条件を満足する優れた担体となることを見いだした。また、更に研究を進めた結果、木材、パルプ、チップ、紙、木質繊維、植物繊維等のセルロース系有機物質も同様に優れた担体となり、コスト等の実用性の点でも満足することを見いだした。すなわち、こうした特定の石炭類やセルロース系有機物質を担体として用いるならば、その他の点では従来と同様な条件及び手法で触媒調製を行っても、所定の活性金属成分を高担持率に分散性よく担持することができ、前記目的を満足する高性能の重質油水素化処理用触媒を容易に得ることができることを見いだした。こうして、本発明者らは、前記各種の重質油の水素化処理に十分な活性及び性能を示す前記目的を満足する優れた水素化処理用触媒を開発することに成功した。

【００１７】つまり、こうして前記特定の可燃性物質を担体として用いて調製した本発明の水素化処理用触媒を実際にスラリー床等による各種重質油の水素化処理に適用したところ、十分な水素化処理活性（水素化脱硫、水素化脱金属、水素化分解等に対する活性）と有用中間留分の収率が得られる上に、固形分（コーク及びスラッジ等）の副生が十分に低減されることが確認された。また、柔軟で可燃性の炭素質物質を担体に用いていることから従来の無機酸化物担体系触媒の場合に比べて灰分の混入が著しく少なくなり、反応後あえて触媒を除去せずに回収した未分解油をその触媒と共にボイラーの燃料として用いても、ボイラーの管壁等への無機物の付着が無視できる程に低減することも確認された。

【００１８】本発明者らは、上記の知見に基づいて本発明を完成するに至った。

【００１９】すなわち、本発明は、無水無灰ベースでの炭素の割合が６５重量％以下である石炭又はセルロース系有機物質に、少なくとも周期表ＶＩＡ族金属の化合物及び／又は周期表ＶＩＩＩ族の鉄族金属の化合物を担持してなることを特徴とする重質油の水素化処理用触媒を提供するものである。

【００２０】また、本発明は、上記本発明の水素化処理用触媒の適用例として、該水素化処理用触媒の存在下で重質油を水素化処理することを特徴とする重質油の水素化処理法を併せて提供するものである。

【００２１】Ａ．水素化処理用触媒とその調製

本発明の水素化処理用触媒は、担体として前記特定の可燃性物質すなわち、無水無灰ベースでの炭素の割合が６５重量％以下である石炭（この特定の石炭を他の一般の石炭と区別すべく、以下、石炭類［Ｉ］と呼ぶことがある。）、あるいはセルロース系有機物質を用いて調製される。

【００２２】本発明の水素化処理用触媒を調製するに際

して担体として用いる前記石炭類［Ｉ］としては、無水無灰ベースでの炭素の割合が６５重量％以下である石炭類であればどのようなものでも適用可能であるが、中でも特に好ましいものとして、泥炭、草炭（例えば、ピートモス等）を挙げることができる。これら各種の石炭類［Ｉ］は、１種のみを使用してもよいし、場合に応じて２種以上のものを混合物等として併用してもよい。

【００２３】ここで、もし、無水無灰ベースでの炭素の割合が６５重量％より大きい炭化度の高い石炭、例えば、無煙炭、半無煙炭、瀝青炭、亜瀝青炭や一般の亜炭や褐炭等を担体とすると、前記所定の活性金属成分を良好な担持状態で担持することが困難であるため、少なくとも従来一般的な担持手法では、劣質な重質油の水素化処理に十分な活性及び性能を有する所望の触媒を得ることは困難である。なお、そのような炭化度が高い一般の石炭を担体として常法によって調製した水素化処理触媒では、たとえ活性及び中間留分の収率の点では満足しても、残留固形分（コーク、スラッジ等）の副生が多くなり本発明の目的を達成することができない。無水無灰ベースでの炭素の好ましい割合は１０～６５重量％、より好ましくは３０～６５重量％である。

【００２４】本発明の触媒を調製するに際して、担体として各種のセルロース系有機物質が使用可能である。該セルロース系有機物質としては、例えば、木材、紙、パルプ、チップ、木質繊維、植物繊維等を挙げることができ、中でも特に、パルプ、チップ、紙などが好ましい。

【００２５】ここで、木材は、針葉樹、広葉樹あるいは草木類等の各種の原木の各種の部分（茎、枝、樹皮など）から得られるものが使用可能であり、これらは、適当なサイズ・形状に加工されたものであれば、生木状のもの、枯木状のもの、あるいはこれらに例えば乾燥、湿潤、温水若しくは熱水処理、スチーム処理、酸処理、塩基処理、ハロゲン化処理、亜硫酸（塩）処理、アルカリ金属塩水溶液、有機溶媒等による洗浄や抽出等の処理、部分酸化処理、水素化処理、硫化処理、乾留等の種々の化学的あるいは物理的処理を施したものなど適宜各種の形態で使用することができる。もちろん、例えば合板等に加工されたものや使用後の回収材、加工工程で副生する端材、オガクズや廃材等を利用してもよい。

【００２６】また、紙やパルプについても同様であり、各種の原料から得られる各種の形態のものが使用可能である。紙について言えば、セルロース性繊維からなるものであれば洋紙、和紙、半合成紙、合成紙、複合紙などどのようなものでもよく、例えば、通常の印刷用のもの、包装用のもの、障子紙、壁紙等の建材用若しくは意匠用のものあるいはトイレットペーパーやティッシュ類等々いずれも使用可能である。また、経済性の点から、適宜、古紙や再生紙、切断等によって副生したクズ紙などを使用してもよい。これらの各種の紙類の中でも、特に、トイレットペーパーやティッシュ類等の担持液が滲み込みやすいものが好適に使用される。パルプも溶解パルプ、製紙用パルプのいずれも使用可能である。

【００２７】前記チップとしては、製材所廃材などを挙げることができる。

【００２８】前記木質繊維としては、各種の木や木材、パルプ、紙等から得られるセルロース性の繊維若しくは繊維束、布状のものなどを挙げることができる。

【００２９】また、前記植物繊維としては、各種の植物を原料とした天然繊維若しくはその加工品（糸や布でもよい）が使用可能であり、例えば、木綿、カポック、パンヤ等の種子毛繊維、コウゾ、ミツマタ、亜麻、黄麻等のジン皮繊維、麻等の葉脈繊維、あるいは、ヤシ、麦わら、ゼンマイ、藤ズル等のその他の系統のものなど各種のものを挙げることができる。

【００３０】なお、前記木材、紙、パルプ、チップ、木質繊維、植物繊維等は、それぞれを単独で担体として使用してもよいし、２種以上を混合物若しくは複合物等として併用することもできる。

【００３１】ところで、前記担体として用いる石炭類［Ｉ］やセルロース系有機物質は、少なくとも触媒調製時に活性金属成分が担持しやすいように、適宜各種のサイズ若しくは形状のものとして使用される。もちろん、その際、用いる反応方式に適合するように、予め、所定のサイズ・形状にして用いてもよい。

【００３２】例えば、石炭類［Ｉ］について言えば、サイズや形状が適当であればもちろんそのまま用いてもよいが、必要に応じて粉砕、裁断、篩別、分級等によって適当なサイズや形状にして用いてもよいし、あるいは、適宜、造粒や成形を施したものを用いてもよい。スラリー床に使用する場合には、単にボールミル等によって微粉状に粉砕したものも好適となる。

【００３３】また、セルロース系有機物質についても同様であり、例えば、木材の場合には、オガクズ状、チップ状など適当なサイズ・形状にして使用すればよい。紙、パルプ、木質繊維、植物繊維等についても、適当なサイズ・形状のチップ状に適宜切断したり、ほぐしたり、あるいは、成形、加工して使用すればよい。

【００３４】なお、前記石炭類［Ｉ］及びセルロース系有機物質は、場合に応じて、担持に先駆けて前記木材についての説明に記載したような各種の化学的処理や物理的処理を施してから用いてもよい。ただし、乾留等によって炭化を進める場合などいずれの場合にも、無水無灰ベースでの炭素の割合が６５重量％以下の範囲になるように炭化度を制御することが必要である。

【００３５】本発明の水素化処理用触媒は、前記各種の石炭類［Ｉ］及びセルロース系有機物質のうちの１種又は２種以上を担体として用い、該担体に少なくとも周期表ＶＩＡ族金属の化合物及び／又は周期表ＶＩＩＩ族の鉄族金属の化合物を担持することによって調製される。このように、担体として前記石炭類［Ｉ］やセルロース

系有機物質を用いる限り、あとは常法に従って前記所定の活性金属成分を担持してもよい。

【００３６】なお、本明細書ではＶＩＡ族金属と鉄族金属を、適時、活性金属と呼んでいる。

【００３７】前記ＶＩＡ族金属としては、モリブデン、タングステン及びクロムを挙げることができ、これらの中でも、通常は、モリブデンやタングステンが好ましい。一方、前記鉄族金属としては、鉄、コバルト及びニッケルを挙げることができる。これらＶＩＡ族金属と鉄族金属のうちどのような金属種を担持するかは、従来と同様に、場合に応じて適宜選定すればよい。

【００３８】一般的には、１種又は２種以上のＶＩＡ族金属種と１種又は２種以上の鉄族金属種を、金属の組み合わせ効果を考慮して適宜組み合わせて用いることが好ましく、特に、例えば、Ｎｉ－Ｍｏ、Ｎｉ－Ｗ、Ｃｏ－Ｍｏ、Ｃｏ－Ｗ、Ｎｉ－Ｍｏ－Ｗ、Ｎｉ－Ｃｏ－Ｍｏ、Ｆｅ－Ｍｏ、Ｆｅ－Ｗ等の組み合わせが好ましいが、必ずしもこれらに限定されるわけではない。

【００３９】場合によっては、１種又は２種以上のＶＩＡ族金属種のみを担持することもあるし、あるいは、１種又は２種以上の鉄族金属種のみを担持することもある。更には、いずれの場合にも、必要に応じて適宜、ＶＩＡ族金属及び鉄族金属以外の他の金属種等を添加してもよい。なお、鉄族金属種のみを担持する場合には、活性の点から、通常、少なくともＮｉを用いることが好ましく、すなわち、この場合の担持金属種としては、Ｎｉ単独、あるいは、Ｎｉ－Ｃｏ、Ｎｉ－Ｆｅ及びＮｉ－Ｆｅ－Ｃｏの組み合わせが好適となる。また、ＶＩＡ族金属種のみを担持する場合には、通常、少なくともＭｏを用いることが好ましく、すなわち、この場合の担持金属種としては、Ｍｏ単独、あるいは、Ｍｏ－Ｗ、Ｍｏ－Ｃｒ及びＭｏ－Ｗ－Ｃｒの組み合わせが好適となる。

【００４０】本発明の水素化処理用触媒における前記活性金属成分の好適な担持量は、担体として使用する炭素質物質の種類や形態、担持する金属の種類、その組み合わせ、あるいはまた、水素化処理する重質油の性状、プロセスの目的等によって異なるので、一律に定めることができないが、通常は、触媒重量（担持乾燥後の触媒の重量）あたりの金属の重量％で計算して、ＶＩＡ族金属（合計量）が０．５～３０重量％の範囲に、かつ、鉄族金属（合計量）が１～５０重量％の範囲になるように選定するのが好ましく、特に、前者を２～１５重量％の範囲に、かつ、後者を２～２０重量％の範囲に選定するのがより好ましい。ここで、ＶＩＡ族金属の担持量が０．５重量％未満であったり、あるいは、鉄族金属の担持量が１重量％未満であると、十分な水素化処理活性が得られないことがある。一方、ＶＩＡ族金属の担持量を３０重量％より大きくしたり、あるいは、鉄族金属の担持量を５０重量％より大きくしても、それ以上の活性の向上は見られず、かえって、活性が低下するなどの支障を生じることがある。

【００４１】なお、前記したようにＭｏ等のＶＩＡ族金属のみを担持する場合やＮｉ等の鉄族金属のみを担持する場合にも、それぞれを、前記同様の範囲に選定するのが好ましいが、一般に、その活性は、ＶＩＡ族金属と鉄族金属を上記の範囲に選定して担持した場合と比較して低くなる傾向がある。

【００４２】以上のように選定した活性金属種（ＶＩＡ族金属及び／又は鉄族金属）を前記所定の担体に担持するに際して、これらの活性金属は、それぞれ、適当な化合物の水溶液等の形態として用いられる。その際の担持手法としても特に制限はなく、後述するように各種の担持方式が適用可能である。

【００４３】すなわち、前記担体に活性金属化合物を担持する際に用いる担持液を調製するに際して、前記活性金属は多種多様な化合物として使用することができる。この担持液は、通常水溶液の形態をとっているが、該担持液の調製に際しては、後述のように場合に応じて適当な添加剤を添加し、その活性金属化合物の溶液性を向上させたり、溶液の安定性を向上させることができるので、用いる活性金属化合物は、必ずしもそれ自体が水溶性のものでなくてもよい。要するに、活性金属種は、できるだけ均一に溶解させた状態で担持に供することが望ましいが、調製原料として用いる活性金属化合物としては、結果としてそのような条件を満たすものであれば、どのような種類及び形態のものでも適用可能である。

【００４４】担持液の調製に際して、前記のＶＩＡ族金属は、例えば、酸化物（MoO_3、WO_3、CrO_3等）、水酸化物若しくは酸素酸（モリブデン酸、タングステン酸、ヘテロポリ酸、水酸化クロム等）、酸素酸塩（例えば、モリブデン酸アンモニウム、タングステン酸アンモニウム、ヘテロポリ酸塩、クロム酸アンモニウム等）、ハロゲン化物若しくはオキシハロゲン化物（例えば、$MoCl_5$、$MoOCl_3$、WCl_6、$WOCl_4$、WO_2Cl、$CrCl_3$、CrO_2Cl_2等）、硫化物（例えば、MoS_2、WS_2等）、シアン化物、硝酸塩［$Cr(NO_3)_3$等］、硫酸塩［$Cr_2(SO_4)_3$等］、酢酸塩等の有機酸塩、アルコキシドなど、また、これらの錯等の錯体類［例えば、ＥＤＴＡ錯体、アセチルアセトナト錯体、ニトロシル錯体、カルボニル錯体等々］、更には、ヒドロゲルやゾル状化合物等のコロイド形態のものなど、様々な種類・形態のものとして、１種あるいは２種以上を使用することができる。

【００４５】これらの中でも、Ｍｏ及びＷについては、通常、MoO_3やWO_3等の酸化物、モリブデン酸やタングステン酸等の酸素酸類、パラモリブデン酸塩、メタモリブデン酸塩、パラタングステン酸塩、メタタングステン酸塩等の酸素酸塩などが好適に使用され、特に、パラモリブデン酸塩、メタモリブデン酸塩、パラタングステン酸塩、メタタングステン酸塩などが好適に使用され

る。なお、これらのモリブデン酸塩、タングステン酸塩には、アンモニウム塩、アルカリ塩等の各種の塩があり、これらはいずれも使用可能であるが、通常は、アンモニウム塩が特に好適に使用される。

【００４６】なお、これらのＭｏやＷの酸化物、酸素酸類あるいは酸素酸塩の中にも、そのままでは水に対する溶解度はあまり大きくないものあるが、そのようなものについても適宜適当な添加剤、例えば有機酸、ＥＤＴＡ等を添加したり、液のｐＨを調整するなどして溶解度や溶解安定性を向上させることができる。

【００４７】一方、前記鉄族金属も、担持液の調製に際して、多種多様な化合物として使用することができ、具体的には例えば、例えば、硝酸塩、炭酸塩、塩基性炭酸塩、硫酸塩、塩化物等のハロゲン化物、硫化物、シアン化物などの無機塩、酢酸塩、酒石酸塩、安息香酸塩等の有機酸塩、酸化物、水酸化物、アルコキシドなど、更にはこれらの錯塩等の錯体類、例えば、アンミン錯体、アコ錯体、ＥＤＴＡ錯体、アセチルアセトナト錯体、カルボニル錯体、ハロゲン酸あるいはハロゲン酸塩等、更には、ヒドロゲルやゾル状化合物、金属コロイド等のコロイド形態のものなど、様々な種類・形態のものとして、１種あるいは２種以上を使用することができる。

【００４８】なお、これらの中でも、コバルト及びニッケルについては、通常、硝酸塩、炭酸塩、塩基性炭酸塩等が好ましく、鉄については、通常、硝酸塩等が好ましい。

【００４９】本発明の水素化処理用触媒は、前記所定の担体に、前記所定の活性金属化合物を担持する限り、他の点については、従来と同様の手法によって調製することができる。ただし、この水素化処理用触媒の場合には、担体として可燃性の物質を用いているので、担持後、通常実施されるような高温での空気等の酸素を比較的多く含有するガスによる焼成は避けた方がよい。言い換えれば、そのような高温で焼成しないでも、この触媒の場合には、後述するように比較的低温での乾燥処理で十分な水素化処理活性が得られるのである。

【００５０】前記担体への活性金属化合物の担持は、例えば、各種の含浸法（真空含浸法、加熱含浸法等）、浸漬法、混練法、スプレー法など公知の各種の担持操作手法に従って好適に行うことができる。

【００５１】なお、前記担持は、前記したように必要に応じて適宜適当な添加成分の共存下で行ってもよい。例えば、担持途上のあるいは担持に供する活性金属化合物の水溶液の安定性を更に向上させて、担持をより均一にかつ安定に行うために、カルボン酸等の適当な有機酸を添加することが好適に採用される。

【００５２】この場合、有機酸としては、各種のものが使用可能であり、具体的には例えば、蓚酸、酒石酸、コハク酸、マロン酸、リンゴ酸、クエン酸、蟻酸、酢酸、プロピオン酸などを例示することができる。これらの有機酸は、必要に応じて、１種又は２種以上添加してよい。

【００５３】その際、添加する有機酸の割合は、使用する担体の乾燥重量１００重量部に対して、例えば、０．１～１００重量部の範囲に選定するのが好ましく、特に、５～５０重量部の範囲に選定するのが好ましい。この割合が上記の基準で０．１重量部未満であると有機酸の添加効果が十分に発揮されず、一方、１００重量部を超えると、活性金属化合物の溶解性が悪くなるなどの理由によって、かえって均一に担持することが困難になることがある。

【００５４】本発明の水素化処理用触媒は、以上のようにして所定の活性金属化合物を担持した後、適宜、乾燥することによって得ることができる。

【００５５】この乾燥温度としては、通常、５０～１５０℃、好ましくは、８０～１２０℃の範囲に選定するのが好適である。この乾燥は、通常、空気雰囲気中で好適に実施される。このような温度範囲ならば、空気中で乾燥しても担体が燃焼する心配がないし、また、多くの場合、この空気中での乾燥だけでも担持した活性金属化合物を活性種に十分に活性化できるからである。なお、この乾燥は、必ずしも空気雰囲気で行わないでもよく、用いた活性金属化合物の種類によっては、例えば、減圧乾燥、あるいは不活性ガス気流中での乾燥によっても十分な活性化がなされるし、また、場合に応じて水素等の還元性ガスや他の適当なガス雰囲気中で乾燥・活性化を行ってもよい。

【００５６】また、必要に応じて、乾燥後、適宜適当な温度で、例えば、窒素等の不活性ガスで処理したり、あるいは、担体が燃焼しない範囲で適当な酸素濃度のガスによって焼成してもよいし、更には、水素や硫化水素あるいはその混合ガス等によって還元若しくは予備硫化等の活性化処理を行ってもよい。

【００５７】こうして調製した本発明の水素化処理用触媒は、各種の重質油、特に前記したような劣質の重質油（超重質油等）の水素化処理に対して、十分な活性を有し、十分な有用中間留分の収率を与える上に、コーク、スラッジ等の残留固形分副生が少ないなど優れた触媒性能を有しており、しかも、担体に柔軟で可燃性の物質を用いているので、スラリー床に用いても装置の摩耗の問題がなく、生成油やその蒸留残油（未分解回収油）への灰分の混入も著しく少なくなり、したがって、触媒を除去しないでも未分解回収油等をそのままボイラー用等の燃料として好適に利用することができるなどの種々の利点を有している。

【００５８】前記本発明の水素化処理用触媒は、必ずしも重質油の水素化処理に限らず、他の一般的のより軽質な含硫炭化水素油の水素化処理にも有効な触媒となるが、特に重質油や超重質油の水素化処理に効果的に使用することができるので、重質油の水素化処理用触媒と称

している。

【００５９】以下に、本発明の水素化処理用触媒の適用例である本発明の重質油の水素化処理法について説明する。

【００６０】Ｂ．重質油の水素化処理法

本発明の重質油の水素化処理法は、重質油の水素化処理、例えば水素化脱硫、水素化脱金属、水素化分解、水素化脱窒素、単純水素化（水添）等を、少なくとも前記本発明の水素化処理用触媒を用いて行うことを特徴としている。

【００６１】ところで、本発明の水素化処理用触媒には、前記したように触媒の組成や調製条件の違い等によって多種多様なものがあるが、これらのうちどのような触媒が好ましいかは、担体として用いる石炭類［Ｉ］又はセルロース系有機物質の種類、活性金属の種類や組み合わせ、担持率などそれぞれの点からすでに説明した。もちろん、実際にどの触媒を用いるかは、場合に応じて適宜最良なものを選定して用いればよい。どの触媒が最良となるかは、例えば、原料として用いる重質油の性状、特に硫黄含有量、沸点範囲若しくは重質度等、反応方式、反応条件、プロセスの目的、例えば、硫黄分をどこまで低減させるか、水素化分解をどの程度進行させ中間留分としてどのような沸点範囲のものを目標とするかなどの諸条件によって異なるので、こうした条件を考慮し、必要に応じて、予備テストを行うなどして適宜最良のもの選定すればよい。

【００６２】すなわち、本発明の方法においては、前記各種の本発明の水素化処理用触媒中から選定された少なくとも１種の触媒の存在下で、重質油を適当な条件で水素ガスと接触させて水素化処理を行う。

【００６３】その際、本発明の触媒は、単独で用いてよいし、２種以上を併用してもよい。

【００６４】原料油として用いる重質油としては、例えば、各種の原油の常圧蒸留や減圧蒸留によって得られる常圧残油、減圧残油等、あるいは、オイルサンド油、石炭液化油等を挙げることができるが、必ずしもこれらに限定されるものではない。なお、場合に応じて、２種以上の性状の異なる重質油を混合したり、あるいは重質油により軽質な炭化水素留分を混合して原料油として用いてもよい。

【００６５】前記水素化処理の反応温度は、通常、３００～５５０℃、好ましくは、３５０～５００℃の範囲に選定するのが好適である。水素圧力は、通常、２０～２００ｋｇ／ｃｍ^{2}Ｇ、好ましくは、５０～１５０ｋｇ／ｃｍ^{2}Ｇの範囲に選定するのが好適である。

【００６６】反応型式としては、特に制限はなく、例えば、固定床、移動床、懸濁床（スラリー床）、沸騰床などいずれも適用可能であるが、熱効率、運転性等の点から懸濁床が特に好適に採用される。なお、懸濁床の場合、回分法や半回分法によってもよいが、通常は、生産性等の点から流通法が好ましい。

【００６７】こうした流通法の場合には、供給液空間速度（ＬＨＳＶ）を、通常、０．０５～５ｈ$^{-1}$、好ましくは、０．２～２ｈ$^{-1}$の範囲に選定するのがよい。

【００６８】水素ガスと原料重質油の供給割合（H_2／原料重質油）は、通常、５０～１０００Ｎｍ^3／ｋｌ、好ましくは、１００～８００Ｎｍ^3／ｋｌの範囲に選定するのが好適である。

【００６９】以上のようにして、上記各種の重質油の水素化処理を好適に行うことができ、それらを、硫黄分、窒素分、重金属分等の不純物含量が十分に少なく、有用中間留分に富んだ性状のよい炭化水素油に効率よく転化することができる。また、この方法によると、残留固形分の副生が少ない、生成油中への灰分の混入がないなど、前記したような、本発明の水素化処理用触媒（可燃性物質を担体する高性能触媒）を用いる種々の利点が発揮される。

【００７０】すなわち、こうして得た生成油（反応混合物）は、触媒を分離しないでも、燃料油等として好適に利用することができる。もちろん、従来法のように触媒を分離して利用してもよい。そのように触媒を分離する場合にも、分離しにくい微細な触媒が残留しても支障ないので簡単な分離操作でも十分であるなどの利点がある。

【００７１】また、通常は、得られた生成油は、蒸留等の常法に従って所望の各種の留分に分離してそれぞれの目的に利用されるが、この場合にも、あえて触媒を分離しないでもよく、例えば、中間留分等の比較的軽質な留分を蒸留等によって分離した際の残油（未分解回収油）中には、触媒と若干の残留固形分（コーク、スラッジ等）が含まれているが、この未分解回収油は、そのままでもボイラー用の燃料として好適に使用することができる。もちろん、この場合にも、いずれかの段階で適宜触媒あるいは触媒と残留固形分（コーク、スラッジ等）を除去してもよい。

【００７２】一方、こうして分留された中間留分は、広くはナフサ～軽油程度の留分、通常は灯油、軽油留分を主成分とし、例えばＦＣＣプロセス等のプロセス用の原料油として、あるいは、性状のよい燃料油等として有効に利用することができる。

【００７３】

【実施例】以下に、本発明の実施例及びその比較例を示し、これらによって本発明を更に具体的には説明するが、本発明はこれらの実施例に限定されるものではない。

【００７４】実施例１

モリブデン酸アンモニウム［$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$］２．６３ｇ、硝酸ニッケル［$Ni(NO_3)_3$］２．６４ｇ、リンゴ酸［HOOCCH（OH）$CH_2$COOH］１．５ｇをイオン交換水に溶解し、全量を４５

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ｍｌに調製し、含浸液を調製した。

【００７５】１ｍｍ以下に篩分けた泥炭（炭化度６０．２重量％）２３．８ｇ（乾燥重量１５ｇ）に前記含浸液を加え、２００℃に熱したサンドバス上で撹拌しながら水分を蒸発させ、所定の活性金属成分等を担持した。

【００７６】次いで得られた担持物を１２０℃で１２時間乾燥後、ボールミルを用いて１時間粉砕した。

【００７７】こうして得た触媒の平均粒径は約１μｍであり、乾燥重量あたり金属としてニッケル３重量％、モリブデン８重量％を含んでいた。

【００７８】この触媒０．８１ｇを表１に示す性状の原料油（アラビアンヘビー減圧残油）８０ｇと共に容量３００ｍｌのオートクレーグに仕込み、４５０℃、１３０ｋｇ／ｃｍ²Ｇの水素加圧下で１時間反応を行い、水素化処理触媒としての活性及び性能等を評価した。この評価結果は他の実施例、比較例と共に表２に示す。

【００７９】実施例２

実施例１において泥炭の代わりに草炭（ピートモス：炭化度５４．７重量％）２４．０ｇ（乾燥重量１５ｇ）を用いた以外は同様にして触媒を調製し、その活性及び性＊能も同様にして評価した。結果は表２に示す。

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【００８０】実施例３

実施例１において泥炭の代わりに紙（トイレットペーパー：乾燥重量あたりの炭素含有量４４重量％）１６．９ｇ（乾燥重量１５ｇ）を用いたこと以外は同様にして触媒を調製し、その活性及び性能も同様にして評価した。結果は表２に示す。

【００８１】比較例１

実施例１において泥炭の代わりに褐炭（炭化度６８．４重量％）１７．９ｇ（乾燥重量１５ｇ）を使用したこと以外は同様にして触媒を調製し、その活性及び性能等を同様にして評価した。結果は表２に示す。

【００８２】比較例２

実施例１において泥炭の代わりに瀝青炭（炭化度８２．７重量％）１５ｇを使用したこと以外は同様にして触媒を調製し、その活性及び性能等を同様にして評価した。結果は表２に示す。

【００８３】

【表１】

性状 ＼ 原料油		アラビアンヘビー減圧残油（ＶＲ－ＡＨ）
比重　（１５／４℃）		１．０１３０
動粘度（ｃＳｔ）　＠１００℃		１７７０
硫黄分（ｗｔ％）		５．０３
窒素分（ｗｔ％）		０．３１２
金属分（ｐｐｍ）	バナジウム	１１５
	ニッケル	３６
残留炭素（ｗｔ％）		２１．６
全水素分（ｗｔ％）		１０．０
アスファルテン分（ｗｔ％）		１１．３

【００８４】　※　※【表２】

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		実施例			比較例	
		1	2	3	1	2
担体		泥炭	草炭（ピートモス）	紙	褐炭	瀝青炭
元素分析 wt％	炭素	60.2	54.7	44.4	68.4	82.7
	水素	5.2	5.4	6.2	4.7	4.7
	窒素	2.5	1.4	0.0	0.5	0.9
	硫黄	0.4	0.3	0.0	0.1	0.9
	酸素	31.8	38.2	49.4	26.3	10.8
	（全て、無水無灰ベースでの値）					
反応成績	中間留分 wt％（174－343℃）	28.3	28.3	28.6	28.5	27.7
	固形分収率 wt％（ヘプタン不溶分）	12.1	9.3	12.2	14.3	20.4
	525℃以下の留分への転化率 wt％	76.5	76.5	76.9	76.2	72.8

【００８５】＜結果の考察＞表２からもわかるように、泥炭、草炭（ピートモス）等の炭化度の低い石炭や紙等のセルロース系有機物質を担体として使用すると、炭化度の高い石炭を使用した場合に比べて反応成績が向上する。特に中間留分の比率が同程度であっても、固形分（コークやスラッジ等）の収率が十分に低減される。

【００８６】

【発明の効果】本発明の水素化処理用触媒は、炭化度が低い石炭やセルロース系有機物質という可燃性で柔軟性があり、安価で、しかも、所定の活性金属成分を十分な高担持率まで分散性よく担持することができるなど良い性質を持っている特定の担体を用いて調製されているので、各種の重質油の水素化処理に対して十分な活性及び性能を発揮する上に、担体の可燃性、柔軟性等に基づく種々の利点を有している。具体的に言えば、本発明の触媒を重質油や超重質油の水素化処理に用いた時、例えば、

（ｉ）有用中間留分の収率及び全体としての水素化処理活性が十分である上に、従来の無機酸化物担体系の水素＊化処理用触媒の場合に問題となっていた、装置の摩耗の問題が解決され、特に、触媒がたとえ微粒子化されても灰分の混入がなくなるので、あえて触媒を分離除去しないでも未分解回収油をそのままボイラー用の燃料として好適に利用することができ、触媒を分離する場合にも操作が簡単でよい；

（ｉｉ）従来提案されている亜炭（ｌｉｇｎｉｔｅ）や瀝青炭といった炭化度の高い石炭を担体として用いて調製された水素化処理用触媒の場合と比べて、同様の条件で比較して、中間留分の収率についてはほとんど同様といってもよいが、全体としての活性が増加する場合が多く、特に、残留固形分の副生が大幅に減少する；など優れた効果を発揮する。

【００８７】また、本発明の重質油の水素化処理は、上記本発明の高性能水素化処理用触媒を用いているので、従来の水素化処理用触媒を用いる場合と比較して、少なくとも上記（ｉ）、（ｉｉ）の点で有利となるので、その工業的価値は極めて大きい。

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